

Construction of a dinuclear cluster containing La(III) and 4-hydroxypyridine-2,6-dicarboxylic acid to modify Keggin-type polyoxometalate

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ABSTRACT

A new polyoxometalate (POM)-based inorganic-organic hybrid compound, $[\text{La}_2(\text{L})_4(\text{H}_2\text{O})_{10}][\text{PMo}_{12}\text{O}_{40}]_2 \cdot 8\text{H}_2\text{O}$ (**1**), in which L = 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid) was prepared via the hydrothermal strategy and characterized by elemental analyses, inductively coupled plasma, Fourier transform infrared spectroscopy, and single-crystal X-ray diffraction. The most remarkable structural characteristic of **1** is that $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ ions inserted in the $\text{La}_2(\text{L})_4$ tongs-like structures through hydrogen bonding. This hybrid extended to the 3D supramolecular structure through hydrogen bonding, so that is supposed $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ polyanions taking part in the supramolecular framework of lanthanum complexes.

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1. Introduction

Nowadays, design and synthesis of novel polyoxometalate (POM)-based inorganic-organic hybrid compounds modified by different metal ions and organic ligands have attracted extensive attention owing to the structural diversities and extensive potential applications, such as selective absorption, electrochemistry, biology, heterogeneous shape-selective catalysis, and nonlinear optical and magnetic functional materials [1–5]. Furthermore, POMs-based hybrids exhibit virtues and polyfunctionality arising from both fragments of POMs and metal-organic clusters. Therefore, structural consideration of this series of compounds including the role of organic and inorganic fragments in the inorganic-organic hybrid structures and the type of interactions among them must be reported accurately.

In recent years, developing inorganic-organic hybrid incorporated plenary Keggin-type POMs has a progressive course [6]. However, compared to many reported inorganic-organic hybrid compounds based on Keggin-type POMs, structures containing phosphomolybdates consider relatively less. Comparison the coordination behaviors of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (abbreviated to PMo_{12})

demonstrated that among the reported inorganic-organic hybrid structures based on PMo_{12} Keggin-type POM (Cambridge structural database version 5.40 (November 2018)), PMo_{12} polyoxoanion mostly have non-covalent interaction (in the large percentage (76%)) and other coordination modes have less percentage [7]. These observations confirm our group results in the investigation of size and negative charge of POMs on the interaction by metal-organic complexes [8,9]. Moreover, as expected PMo_{12} units due to the less negative charge and smaller size have non-covalent interaction via their oxygen-reach surfaces in the inorganic-organic hybrid structures [10–12]. In this regard, these weak non-covalent interactions play an important role in the formation of supramolecular assemblies in the POM-based hybrids [13]. Although in the meantime, a few interesting structures were reported that twelve oxygen atoms of PMo_{12} involved in coordination [14].

An intelligent strategy to construct POM-based hybrids is to employ the lanthanoid-N-heterocycle carboxylic acid complexes as linkages beside Keggin POM structural units, yielding a variety of POM-based hybrids [15–20]. Accordingly, some lanthanoid-N-heterocycle carboxylate inorganic-organic hybrids are reported based on PMo_{12} polyanion [21–23]. Historically, many metal-organic complexes are reported based on chelidamic acid but especially, the POM-chelidamic acid hybrids have been rarely studied [9,24,25]. Such N-heterocycle carboxylic acid ligands can be

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deprotonated to the carboxylate anions and act as chelating or bridging ligands. Continuing this approach, we utilized 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid), lanthanum ion and PMo_{12} heteropoly for the construction of POM-based inorganic-organic hybrid for the structural comparison with similar compounds and effect of any of fragments in the final architecture. Therefore we synthesized and characterized a new lanthanum-based inorganic-organic hybrid, formulated as $[\text{La}_2(\text{L})_4(\text{H}_2\text{O})_{10}] [\text{PMo}_{12}\text{O}_{40}]_2 \cdot 8\text{H}_2\text{O}$ (**1**), in which L = chelidamic acid.

2. Experimental

2.1. Materials and physical measurements

Chelidamic acid hydrate was obtained from Sigma–Aldrich (95% purity) and used without further purification. All other reagent chemicals were commercially purchased from Merck and used without further purification. The infrared spectra were recorded in the range of $4000\text{--}600\text{ cm}^{-1}$ on a Buck 500 scientific spectrometer as KBr discs. The elemental analyses (C, H, and N) were performed on a Thermo Finnigan Flash model 1112 EA microanalyzer.

2.2. Synthesis of compound **1**

A mixture of $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (182 mg, 0.1 mmol), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (108 mg, 0.25 mmol), chelidamic acid (46 mg, 0.25 mmol) and deionized water (10 ml) was stirred for about 30 min in air. Finally, the pH was adjusted to 1.5 with aqueous NaOH solution. The mixture was then transferred into a 30 ml Teflon-lined stainless-steel autoclave and kept at $130\text{ }^\circ\text{C}$ for 3 days. After slow cooling at a rate of $5\text{ }^\circ\text{C h}^{-1}$ to room temperature, crystals of the complex **1** could be isolated as pale-yellow crystals in 44% yield (based on PMo_{12}). Anal. Calc. For $\text{C}_{28}\text{H}_{56}\text{La}_2\text{Mo}_{24}\text{N}_4\text{O}_{118}\text{P}_2$: C, 6.75; H, 1.13; N, 1.13; La, 5.6; Mo, 46.2%. Found: C, 6.49; H, 1.26; N, 1.00% La, 5.4; Mo, 45.7%. IR (selected bands, cm^{-1}): 3454 (bs), 1732 (w), 1609 (s), 1485 (w), 1416 (m), 1350 (w), 1240 (w), 1126 (w), 1064 (s), 1022 (w), 967 (s), 882 (m), 787 (m).

2.3. X-ray crystallography

A pale-yellow column-like single crystal of **1** was used for the X-ray crystallographic analysis. The X-ray intensity data were collected on a Bruker Smart APEX CCD system equipped with a graphite monochromator and a Mo- K_α fine-focus sealed tube ($\lambda = 0.71073\text{ \AA}$) at 150 (2) K . Data were corrected for absorption effects using the multi-scan method (SADABS). The structure was solved by direct methods (SHELXT) and refined F^2 by full-matrix least-squares method using the SHELXL-2014/7 program package [26,27]. The crystallographic data and structure refinements for **1** is demonstrated in Table 1. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number 2000687.

3. Results and discussion

3.1. Synthesis and infrared spectroscopy

Generally, the one-pot reaction system is regarded as an unknown process, in which many factors can affect the structure and quality of the final product. In this work, compound **1** was obtained under hydrothermal reaction conditions. We deduce that the influence of the polyoxoanion on the final structure of compound **1** may arise from the difference in pH values and the mole ratio of the reactants. If the pH value of the reaction is higher than 2, crystals of

Table 1

X-ray diffraction crystallographic data and structure refinements for **1**.

Chemical formula	$\text{C}_{28}\text{H}_{56}\text{La}_2\text{Mo}_{24}\text{N}_4\text{O}_{118}\text{P}_2$
Formula weight (g/mol)	4979.22
Crystal size (mm)	$0.29 \times 0.14 \times 0.08$
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	13.6801 (16)
<i>b</i> (Å)	25.144 (3)
<i>c</i> (Å)	17.926 (2)
α, γ (°)	90
β (°)	107.040 (2)
<i>V</i> (Å ³)	5895.4 (12)
<i>Z</i>	2
μ (mm ⁻¹)	3.33
<i>F</i> (000)	4768
<i>D</i> _{calc} (g/cm ³)	2.843
Temperature (K)	150 (2)
Reflections collected	113,879
GOF on F^2	1.044
R_1^a, wR_2^b [$I > 2\sigma(I)$]	0.0414, 0.1140
R_1, wR_2 (all data)	0.0532, 0.1188

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{\sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2\}^{1/2}$.

the lanthanum complexes form without Keggin-type POMs. The molar ratio of $\text{La}(\text{NO}_3)_3$ relative to $\text{H}_2\text{pydc-OH}$ and the PMo_{12} was kept in 5: 5: 2 for preparing the hybrid compound of **1**.

In the IR spectrum of compound **1** (Fig. 1), four characteristic asymmetric vibration bands of the α -Keggin $[\text{PMo}_{12}\text{O}_{40}]^{4-}$ poly-anions corresponding to $\nu_{\text{as}}(\text{P-O})$, $\nu_{\text{as}}(\text{Mo-O}_t)$, $\nu_{\text{as}}(\text{Mo-O}_b\text{-Mo})$ and $\nu_{\text{as}}(\text{Mo-O}_c\text{-Mo})$ are observed at 1064, 967, 882 and 787 cm^{-1} , respectively. The sharp bands in the region of $1732\text{ to }1400\text{ cm}^{-1}$ are ascribed to the vibrations of the $\text{H}_2\text{pydc-OH}$ molecules. The vibration band at 1732 cm^{-1} is indicative of the presence of COOH groups in chelidamic acid ligand. The hydroxyl oxygen atom of the organic ligand by having an absorption band on the 1240 cm^{-1} is also non-coordinated. The wide band around 3400 cm^{-1} ascribed to the characteristic band for water molecules and strong hydrogen bonding.

3.2. Crystal structure determination

The single crystal X-ray diffraction studies reveal that compound **1** belongs to the monoclinic $P2_1/n$ space group. As shown in Fig. 2, the asymmetrical unit of **1** contains one La(III) ion, bearing nine-coordinated mono-capped square antiprism geometrical configuration, one PMo_{12} polyanion, and two organic ligands. The La^{III} ion is ligated by four oxygen atoms of two organic ligands (O1, O2, O6, O7) with La–O bond lengths about 2.480 (4)–2.769 (4) Å and five oxygen atoms derived from five coordinated water molecules. Two bottom planes around the La(III) ions including two series of oxygen atoms (O1, O2, O6, O14) and (O7, O11, O13, O15) have a dihedral angle as 8.68° and distances between La(III) ion and two planes are 1.414 and 0.883 Å, respectively. These data confirm the distortion of mono-capped square antiprism geometry. The coordination mode of chelidamic acid ligands in this compound is among the few cases that nitrogen atom of pyridine ring does not incorporate in the coordination bond with lanthanoid centers and only two vicinal oxygen atoms belonging to one carboxylic group are connected to lanthanoid centers in the crystal structure [28–30].

As the literature shows, among the complexes of lanthanoid ions with chelidamic acid or 2,6-pyridinedicarboxylic acid, some of them demonstrate dinuclear complexes. In all of the crystal structures, the organic ligand performs chelating and bridging roles [31–34]. While in this dinuclear compound, half of the chelidamic

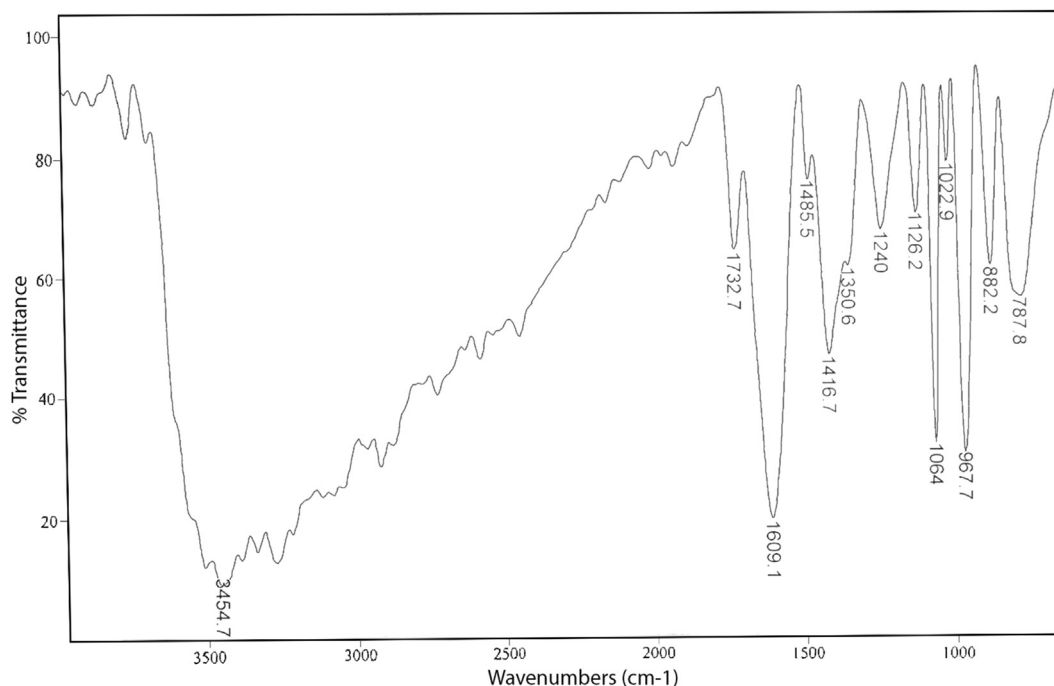


Fig. 1. IR spectrum of 1.

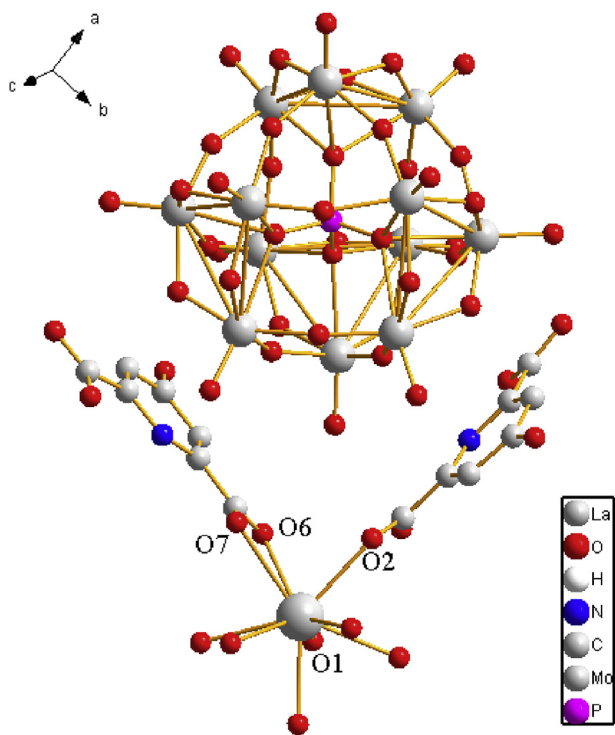


Fig. 2. The asymmetric unit of 1. Lattice water molecules and H atoms are omitted for clarity.

acid ligands act as bridging agents and the other chelidamic ligands act as chelating agents. Just due to the coordination of La–O1 and La–O2 (Fig. 3a), the La^{III} atoms are bridged by two organic ligands to fabricate a cationic metal-organic [La(H₂O)₅(L)]⁶⁺ dimeric structure with La···La distance of 5.211 Å. Furthermore, La–O bond lengths are 2.480 (4) and 2.503 (4) Å for the La–O1 and La–O2

respectively (Fig. 3a). The other coordination spheres of lanthanum center are occupied by two oxygen atoms of one carboxylate moiety (O6, O7) belonging to chelating organic ligand and water molecules (O11, O12, O13, O14, O15). The average La–O distance (2.492 Å) of the linkage mode is smaller than the chelating La–O distance (2.658 Å) of the ligands. This observation is agreed with similar results of another crystal structure containing La-chelidamic acid complexes [35]. Furthermore, the average La–O distance between chelating carboxylate moiety and lanthanum center, in the complex 1 is greater than other reported crystal structures that chelidamic acid act as tridentate chelating mode coordinated to lanthanum centers [31,36]. This result is related to the stronger interaction between metal centers with tridentate organic ligands compared to similar bidentate organic ligands. The hydrogen bonding between PMO₁₂ anions and cationic tongs-like [La₂(L)₄(H₂O)₁₀]⁶⁺ complex beside the electrostatic interactions fortify the dimeric structure (Fig. 3b).

The inorganic [PMO₁₂O₄₀]³⁻ polyanion exhibits typical α -Keggin structural features and low distorted PO₄ fragment encapsulated by the [W₁₂O₃₆] polyoxoanion. The P–O distances are 1.531(4)–1.542(4) Å, and the O–P–O angles are in the range of 108.7(2)–109.8(2)° thereby indicating that the PO₄ unit is nearly a regular tetrahedron. The Mo–O bond length due to the various situation of the oxygen atom in the four {Mo₃O₁₃} triad belonging to a [PMO₁₂O₄₀]³⁻ polyoxoanion has three different quantities. Thus, the Mo–O_t bond lengths [1.673(4)–1.686(4) Å] are the shortest, then W–O_b has [1.807(4)–2.035(4) Å] bond length and finally the longest bond length [2.407(4)–2.453(4) Å] belong to Mo–O_c bonds. The Mo–O and P–O distances in this compound is comparable to the reported values [12,37].

It should be mentioned since in the compound 1 the hydrogen bonding network stabilizes the crystal structure, water molecules whether coordinated to lanthanum centers or not, help to the fortification of architecture. In this compound, only electrostatic interactions and hydrogen bonds are involved between the metal-organic and the PMO₁₂ anions, with no covalent bonding. These observations can be related to smaller size and the less negative

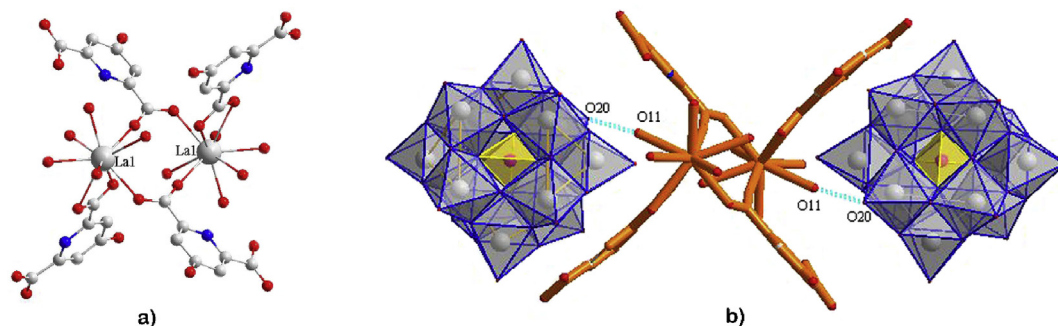


Fig. 3. a) The coordination diagram of La(III) atoms in compound 1. b) Adjusting of PMo_{12} heteropoly in the tongs-like $[\text{La}(\text{H}_2\text{O})_5(\text{H}_2\text{pydc-OH})]^{3+}$ complex by hydrogen bonding in the dimeric structure. Lattice water molecules and H atoms are omitted for clarity.

charge of the PMo_{12} anions in this crystal structure relative to $\text{BW}_{12}\text{O}_{40}^{2-}$ and $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions. Somehow, $[\text{BW}_{12}\text{O}_{40}]^{5-}$ and $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions with various coordination modes are connected to lanthanoid complexes in the crystal structures of inorganic-organic hybrids with chelidamic ligand [9,24,25]. All of the hydrogen bonds are listed in Table 2.

Two PMo_{12} anions exist for the one tongs-like of $\text{La}_2(\text{L})_4$ fragment while having distances 8.899 Å with neighboring lanthanum centers. The PMo_{12} polyoxoanion through one oxygen atom (O11–H11b ... O20 distance and angle is 2.858 (5) Å and 139.88 (15)° respectively) is linked to a coordinated water molecule in the dinuclear discrete structure. Whereas two other oxygen atoms of the polyoxoanion, a terminal oxygen atom (O24) and a bridging oxygen atom (O51), are interacted to lattice water molecules and connected to adjacent $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ fragment. Furthermore, this hydrogen bonding chain reinforced by connection to the oxygen atoms of the hydroxyl groups of organic ligands (O5–H5...O61). Indeed, the oxygen atom of one water molecule (O61) acts as a bridge between two PMo_{12} and neighboring lanthanum complex (Fig. 4).

As shown in Fig. 5a and b, these similar structural units by two types of hydrogen bonding resulting from PMo_{12} heteropoly (O20 and O51) are gathered together to construct a 2D squareness framework with PMo_{12} centrality (Fig. 5c). The whole structure by contributing to another terminal oxygen atom of PMo_{12} (O24) and spreading a broad network of hydrogen bonds is extended to the 3D supramolecular architecture (Fig. 5d).

4. Conclusions

In conclusion, an inorganic-organic hybrid assembled from

Table 2
Hydrogen bond parameters (Å) for compound 1.

D—H...A	D—H	H...A	D...A	D—H...A
O5—H5...O61	0.84	1.71 (1)	2.516 (11)	161 (1)
O11—H11b...O20 ⁱ	0.87	2.14 (1)	2.858 (5)	140 (1)
O13—H13b...O63 ⁱⁱ	0.87	1.94 (2)	2.751 (15)	154 (1)
O15—H15a...O56 ⁱⁱ	0.87	2.07 (1)	2.806 (7)	142 (1)
O57—H57b...O63	0.87	2.17 (2)	2.81 (2)	130 (1)
O60—H60b...O51 ⁱⁱⁱ	0.87	2.21 (1)	2.847 (10)	130 (1)
O61—H61a...O60	0.87	1.73 (1)	2.524 (14)	151 (1)
O61—H61b...O24 ^{iv}	0.87	2.36 (1)	2.894 (11)	120 (1)
O62—H62a...O4	0.87	2.12 (2)	2.863 (16)	144 (1)
O64—H64b...O62	0.87	2.02 (2)	2.63 (2)	126 (1)
O65—H65b...O5	0.87	2.22 (2)	2.864 (16)	130 (1)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x-1/2, -y+1/2, z+1/2$; (iii) $x-1/2, -y+1/2, z-1/2$.

(iv) $-x+1/2, y+1/2, -z+1/2$.

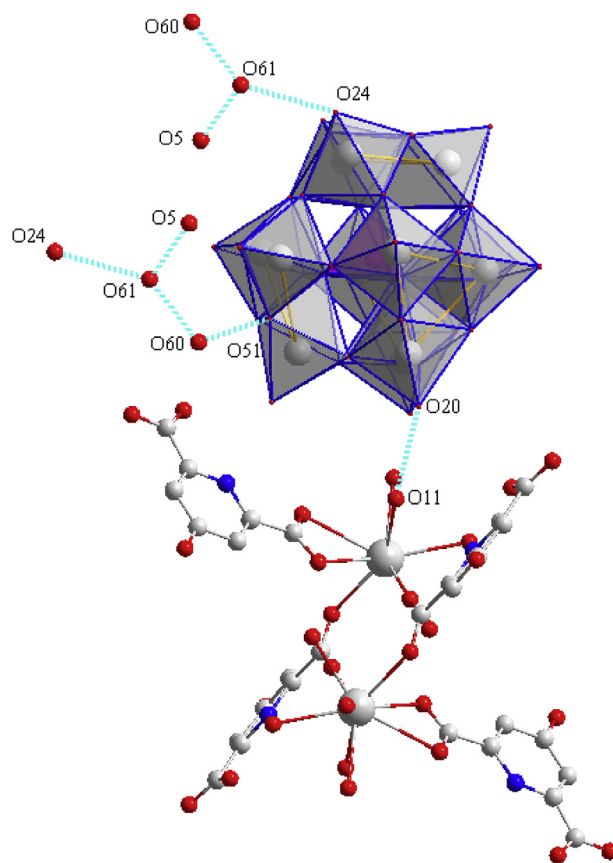


Fig. 4. A View of hydrogen bondings between $\text{La}_2(\text{C}_7\text{H}_5\text{NO}_5)_4$ fragment and PMo_{12} heteropoly in the inorganic-organic hybrid. Dashed lines represent the hydrogen bonds. Hydrogen atoms are omitted for clarity.

plenary Keggin-type POM unit and metal-organic complex containing chelidamic acid organic ligand and lanthanum center has been synthesized and characterized. This discrete structure consists of dinuclear lanthanum complexes that further connected to the Keggin-type POM. Although, POM fragments do not coordinate with metal centers but their oxygen-rich surfaces are incorporated in strong hydrogen bonding. Therefore, the hydrogen bonding network extended the dimeric structure to the 3D supramolecular architecture. These results confirm that the inorganic-organic hybrid materials based on polyoxometalate can be as effective sorbents to sample treatment of complex matrices. The interaction and stabilization of organic moieties by POMs has been extensively

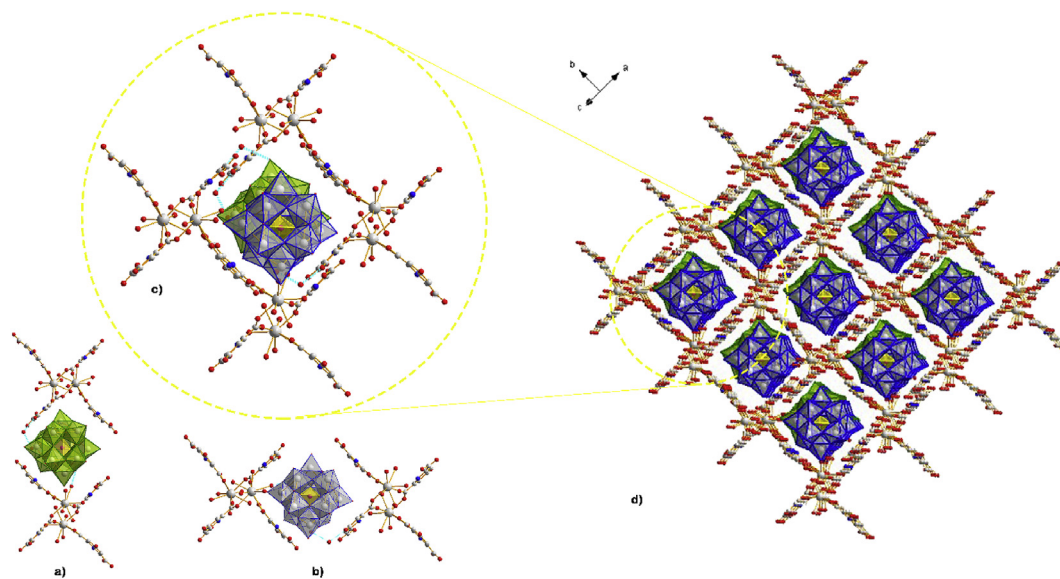


Fig. 5. a, b) Structural fragments of spreading hydrogen bonds that lead to connecting $[\text{La}(\text{H}_2\text{O})_5(\text{H}_2\text{pydc-OH})]^{3+}$ complexes in 1D. c) Squareness units are composed of overlapping two structural units (a and b) and the expansion it to the 2D structure. d) A Side view of the 3D supramolecular structure of compound 1. Lattice water molecules and H atoms are omitted for clarity.

documented including by non-electrostatic interactions such as hydrogen bonding and cumulative stability afforded by multiple weak interactions such as van der Waals interactions and dispersion forces.

CRediT authorship contribution statement

Fatemeh Taghipour: Investigation, Writing - original draft, Writing - review & editing, Project administration. **Masoud Mirzaei:** Investigation, Writing - original draft, Writing - review & editing, Project administration.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2020.128594>.

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